

SRS Sludge Heel Chemical Cleaning Project



We Put Science To Work

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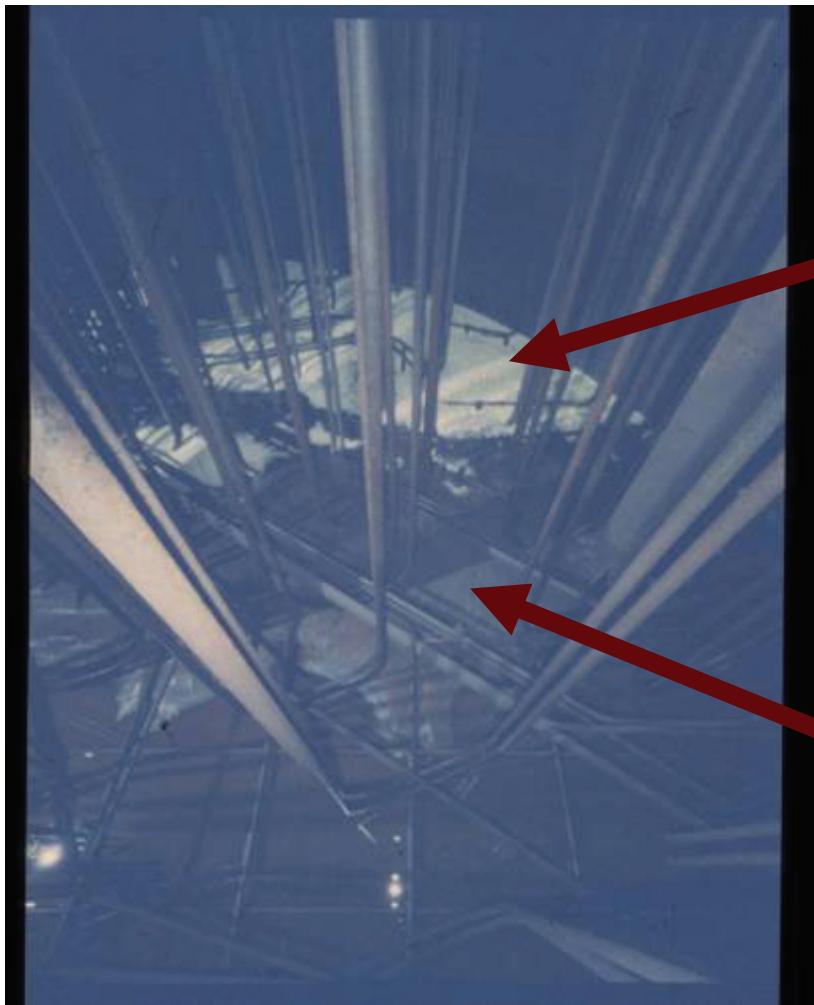
Introduction

- Typically, bulk sludge is removed by slurry and decant operations
- Residual heel may remain that cannot be removed by slurring
- Historically, oxalic acid used to dissolve sludge heel
- Although the total amount of corrosion may be insignificant for a short contact time, a significant amount of hydrogen may generate from the corrosion reaction
- Future sludge tank chemical cleaning will use 8 wt % oxalic acid to dissolve and loosen sludge heel
- Oxalic acid/sludge mixture transferred to receipt tank and neutralized

Test Program

- Characterize sludge and “snowbank” samples
- Determine:
 - effectiveness in dissolving sludge
 - hydrogen generation rate
 - generation rate of other gases
 - carbon steel corrosion rate
 - impact of mixing on chemical cleaning
 - impact of temperature
 - determine the types of precipitates formed during the neutralization process
- Simulant Demonstration
- Actual Waste Test

March 2006 View



"snow bank"

sludge

Sludge Sample Characterization

- Dropcore Probe Sample - October 2006
 - (designed by T. Nance and N. Vrettos)
- Obtained ~300 g of moist sludge solids
- Characterization
 - XRD and CSEM
 - Solids digested by two methods
 - Extensive chemical and radionuclide characterization of digested solids
- Also characterized receipt tank supernate sample (representative of sludge tank supernate).



Sludge Core Sample

Snowbank Sample Characterization

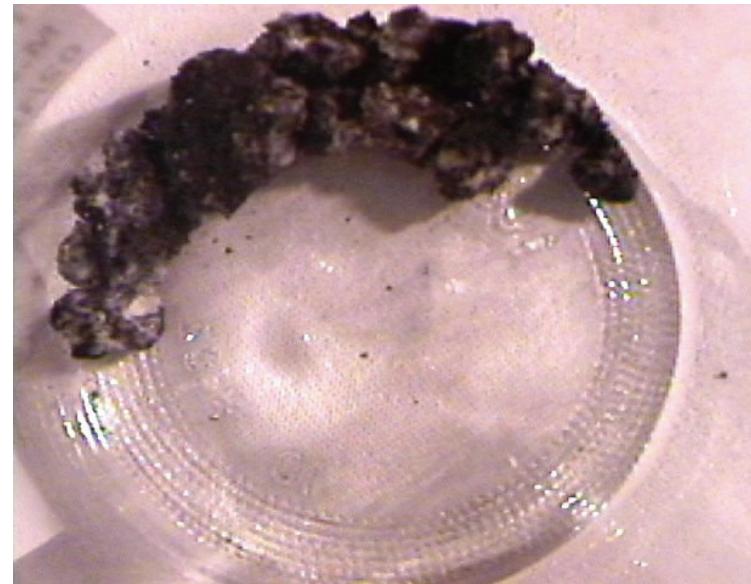
- **SuperSnapper Sample - February 2007**
 - (designed by T. Nance and N. Vrettos)
- **Coating on sludge, not “snowbank”**
- **Obtained ~230 g of mostly sludge solids**
- **Picked 12 g of white solids from sample**
- **Characterization**
 - XRD and CSEM
 - Water Solubility/Separation
- **Solids determined to be water soluble allowing separation from sludge.**



Snowbank SuperSnapper Sample

Snowbank Sample Characterization

- **XRD Results**
 - hydrated sodium carbonate and bicarbonate
 - some aluminum hydroxide also
- **CSEM Results**
 - Highly Crystalline
 - Na, C, O consistent with sodium carbonates
- **No further characterization required by customer.**



White Solids picked from Sample
(coated with sludge)

Scaled Demonstrations with Simulated Sludge

- Simulates planned operation for addition of 8% oxalic acid through transfer to receipt tank
- Simulated sludge with uranium
- Scaled to approximately match:
 - mixing energy of re-circulating pump
 - metal surface area to acid ratio
 - 20:1 acid to sludge heel
 - oxygen (air) turnover rate
 - transfer rate
- Test design:
 - 25, 50 and 75 °C
 - Mixed and un-mixed in heel tank
 - Measure gas generation, hydrogen in off-gas, dissolution behavior, in situ corrosion rates, mixing behavior, characterization of solid residues



Simulant Demonstration Test Plan

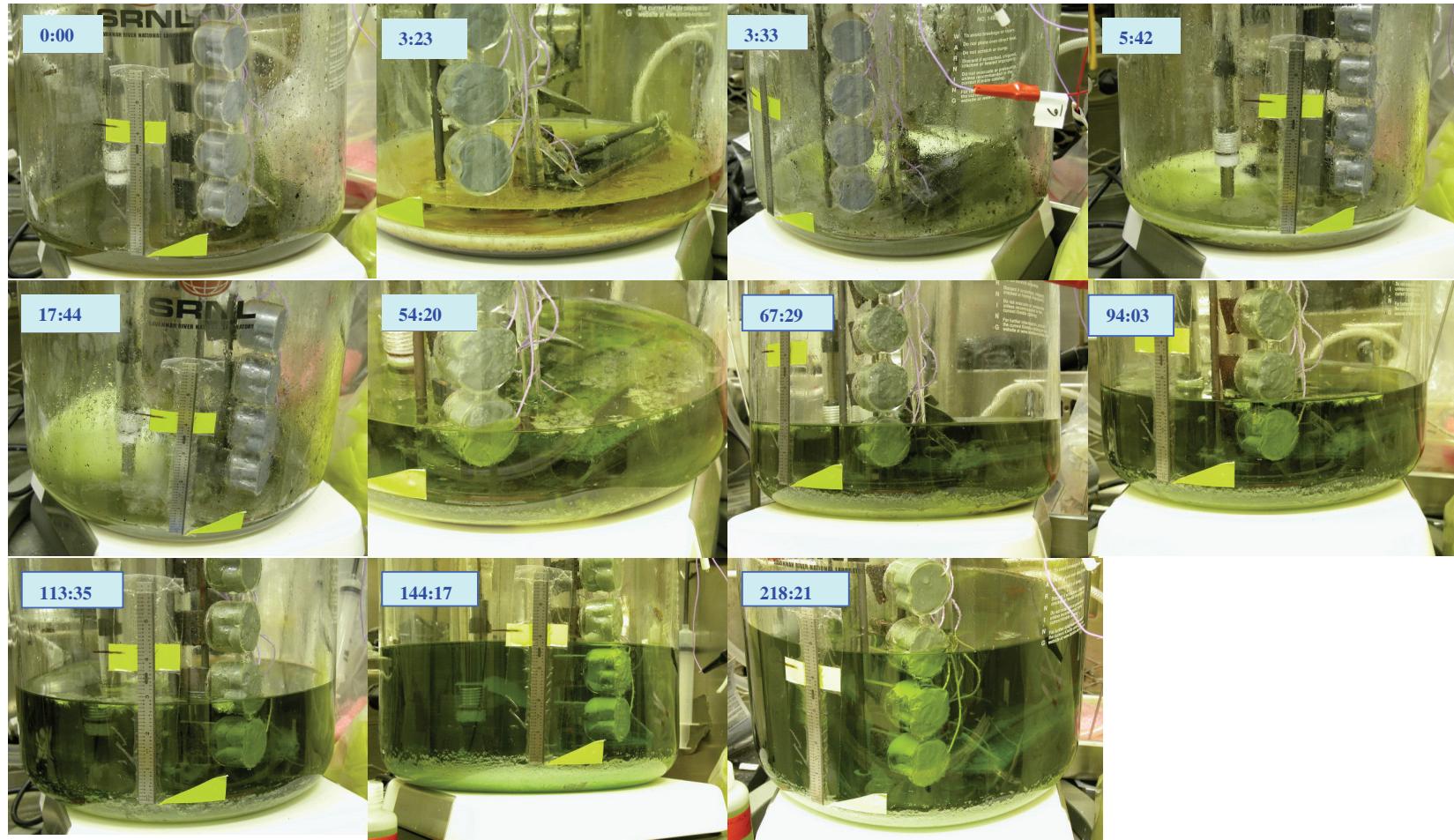
- Add (Depleted Uranium) sludge to Dissolution Vessel
- Add Supernate
- Heat to 25, 50 or 75 °C
- Add acid (typically 7 day addition 0.75 mL/min)
- Turn on agitator as liquid covers blades (as appropriate to experiment)
- Stop acid addition and “soak” for 50 hours
- Fill Receipt Vessel with 5 liters simulated supernate
- Transfer specified amount (1.5-3 liters) to Receipt Vessel

Simulant with DU Sludge Experimental Setup

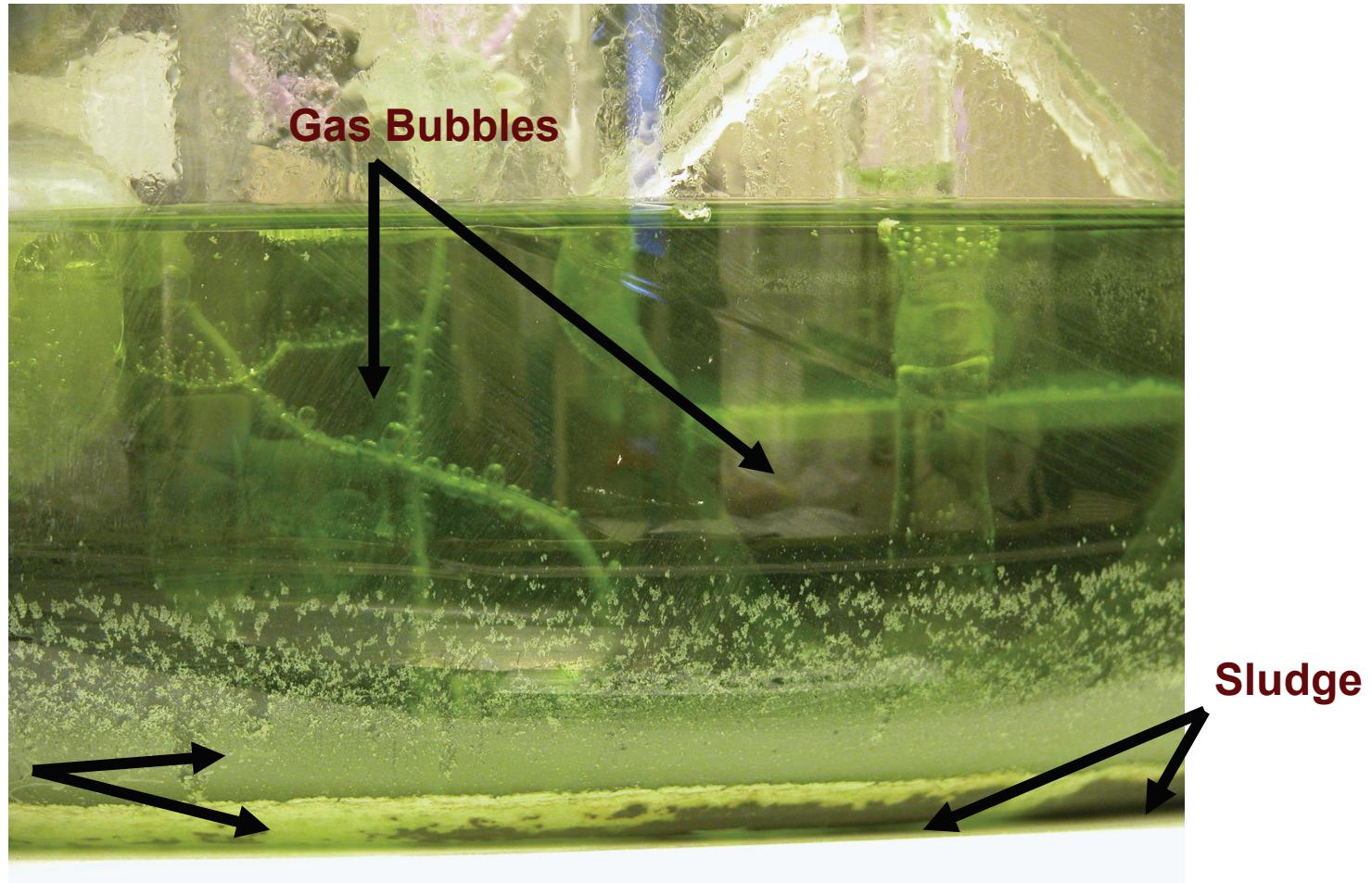


SRS Sludge Tank Chemical Cleaning Project

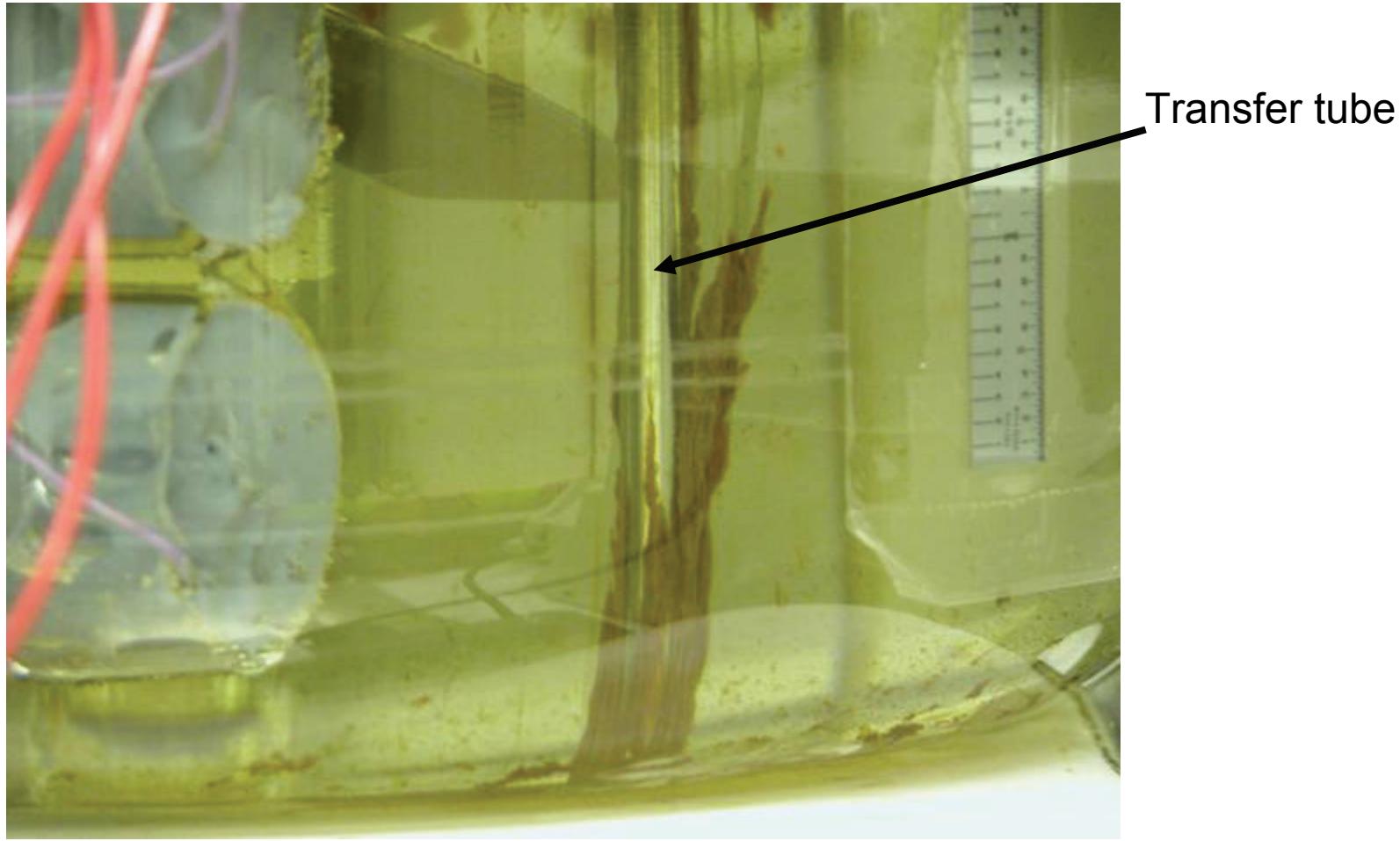
Progression of Dissolution in 25 °C/Unmixed Test from Start of Acid Addition



Gas Generation During OA Addition to Dissolution Tank



Precipitation of Solids during Transfer



Precipitation immediately upon transfer of tank contents

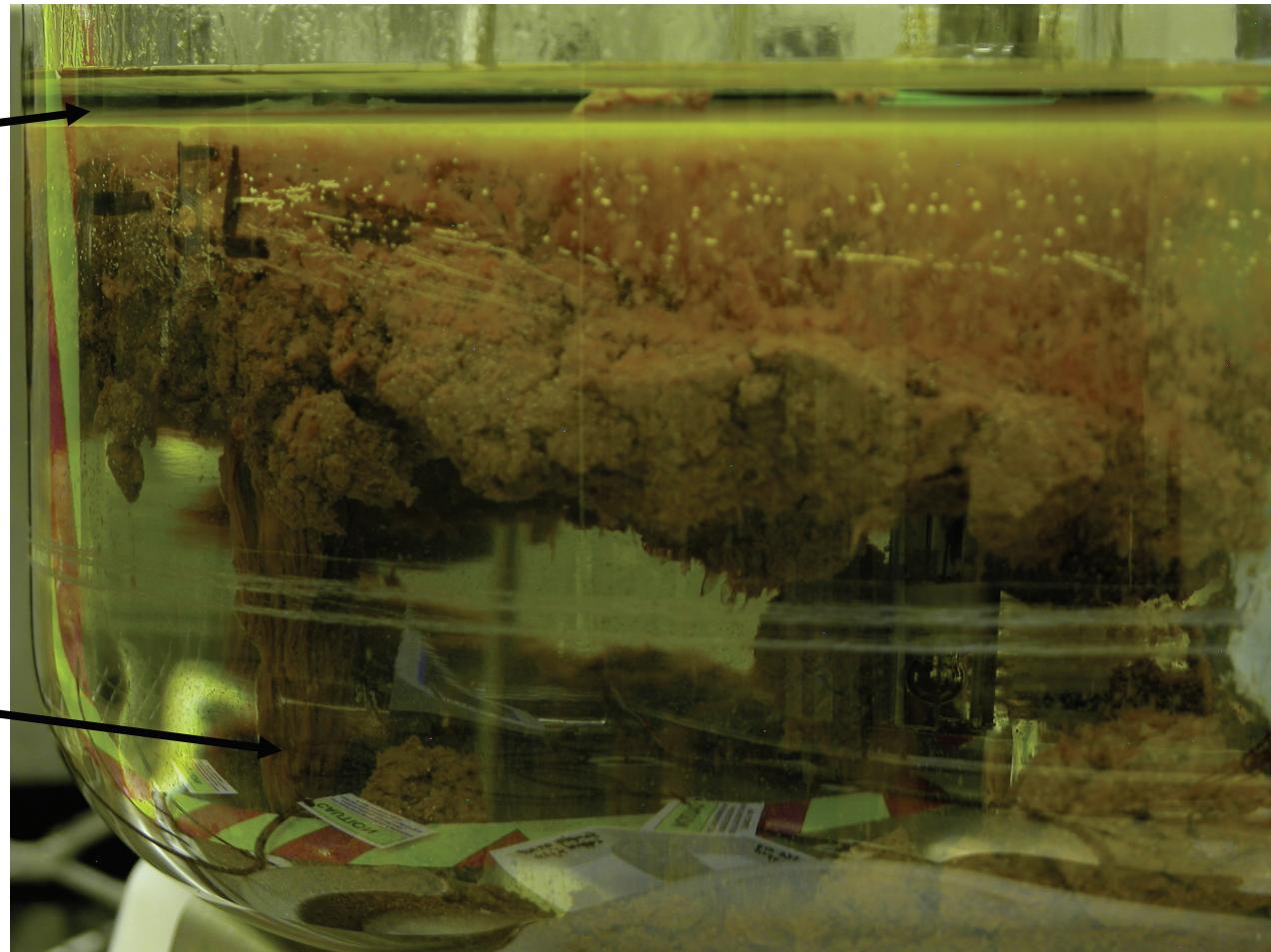
SRS Sludge Tank Chemical
Cleaning Project

Receipt Vessel Solids and Floating Layer

Building of floating layer



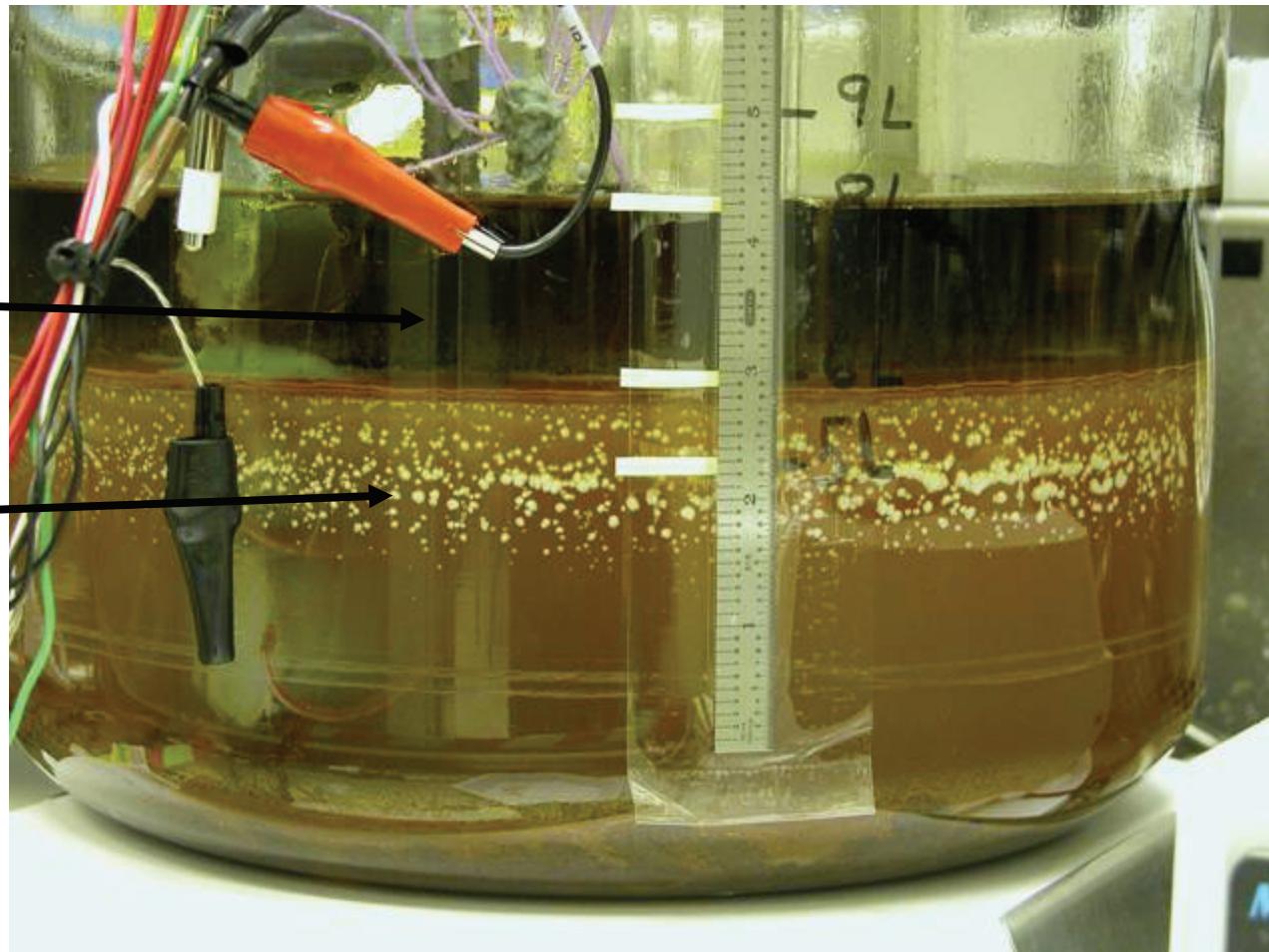
Transfer tube



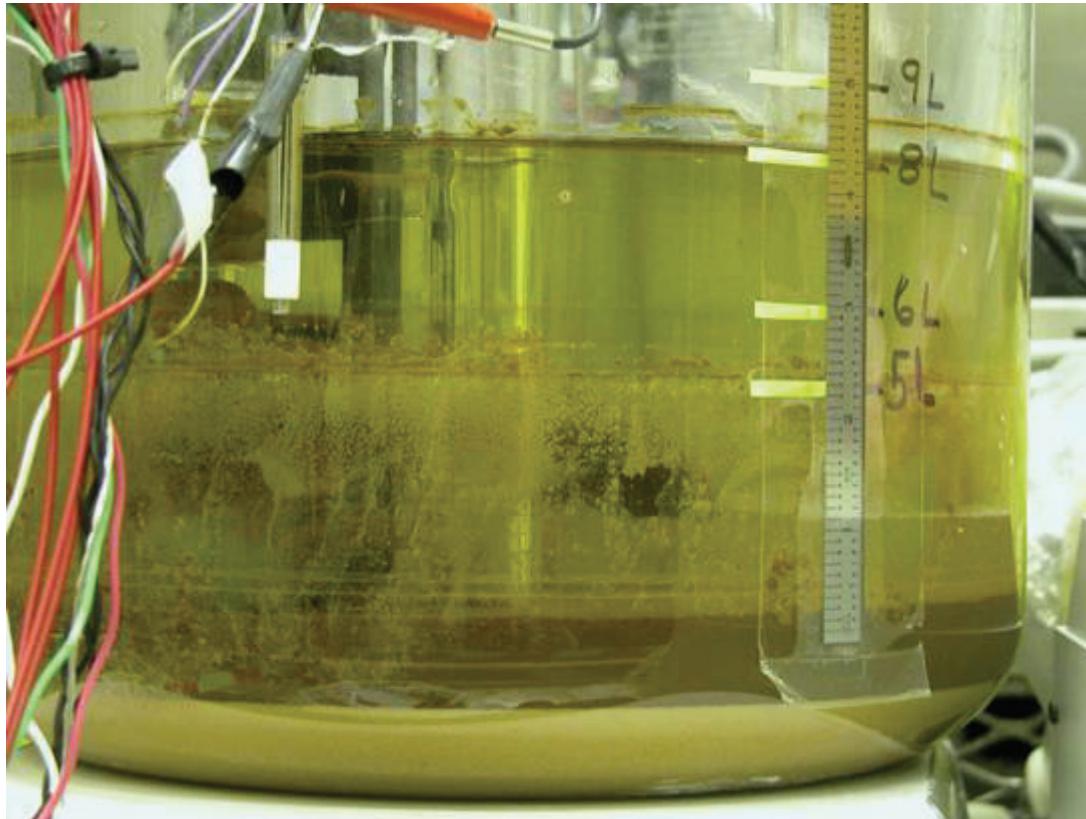
Receipt Vessel Contents Upon Completion of Transfer

Floating layer
pH <2

Formation of
White solids
Liquid region
pH >12



Dissolution Vessel after Mixing and Settling of Solids



Dried Solids from Dissolution and Neutralization Vessels

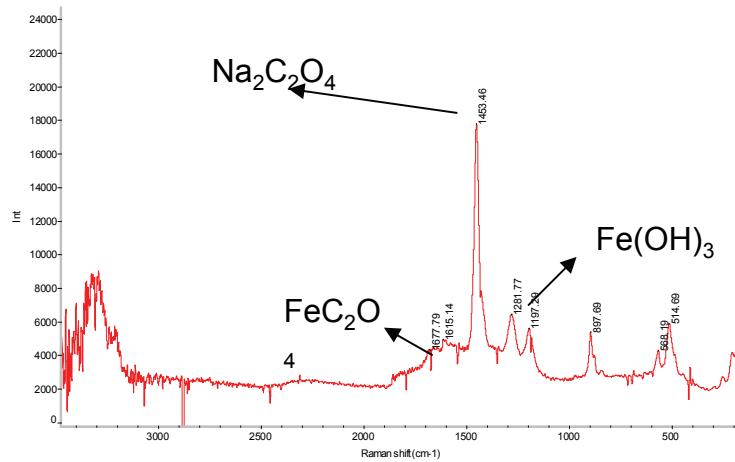
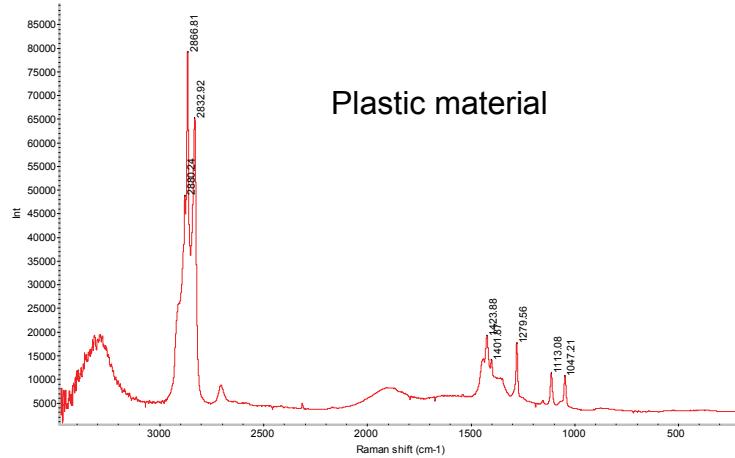
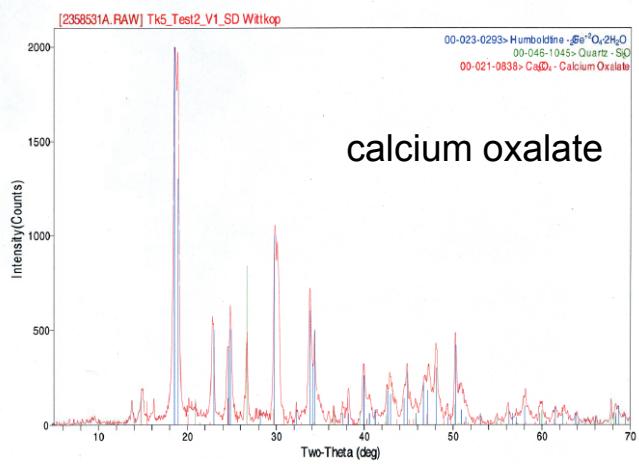


Dissolution Vessel

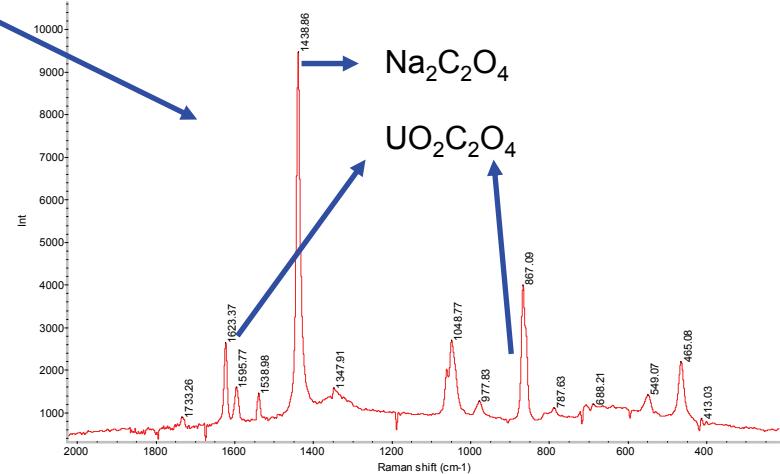
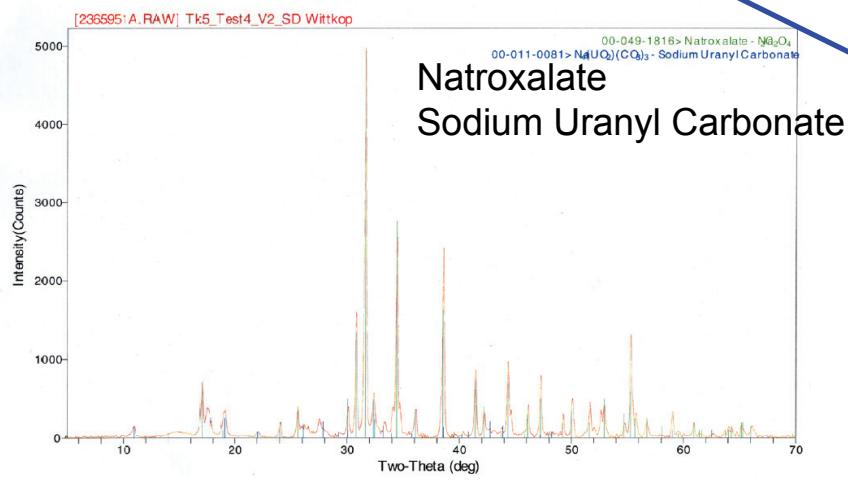
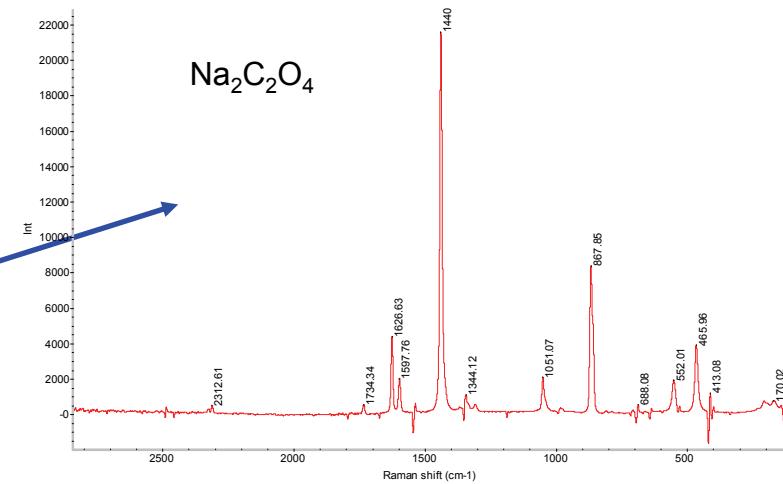
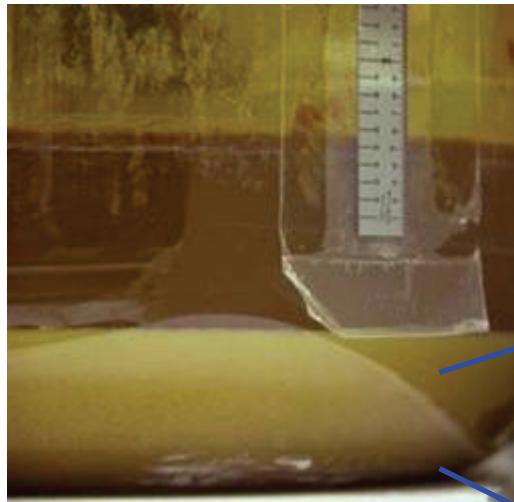


Neutralization Vessel

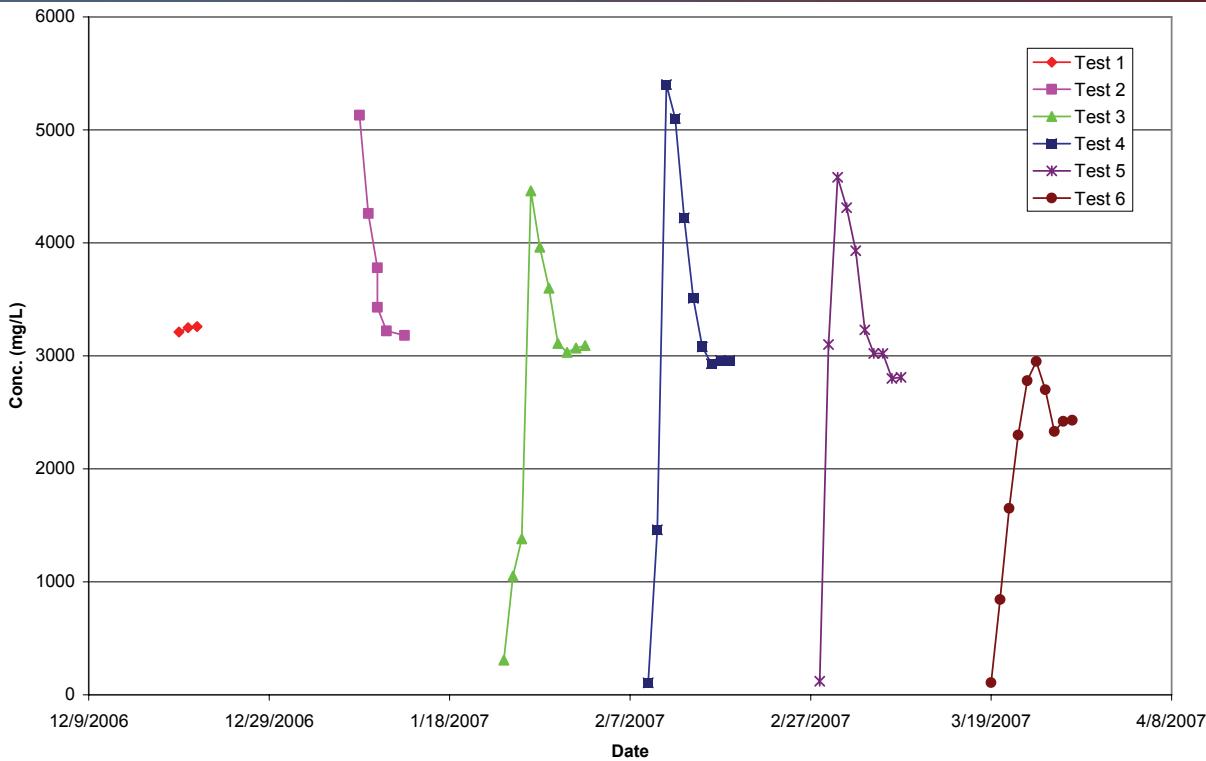
XRD and FT-Raman of Solids from Dissolution Vessel (75 °C, mixed)



Receipt Vessel Settled Solids



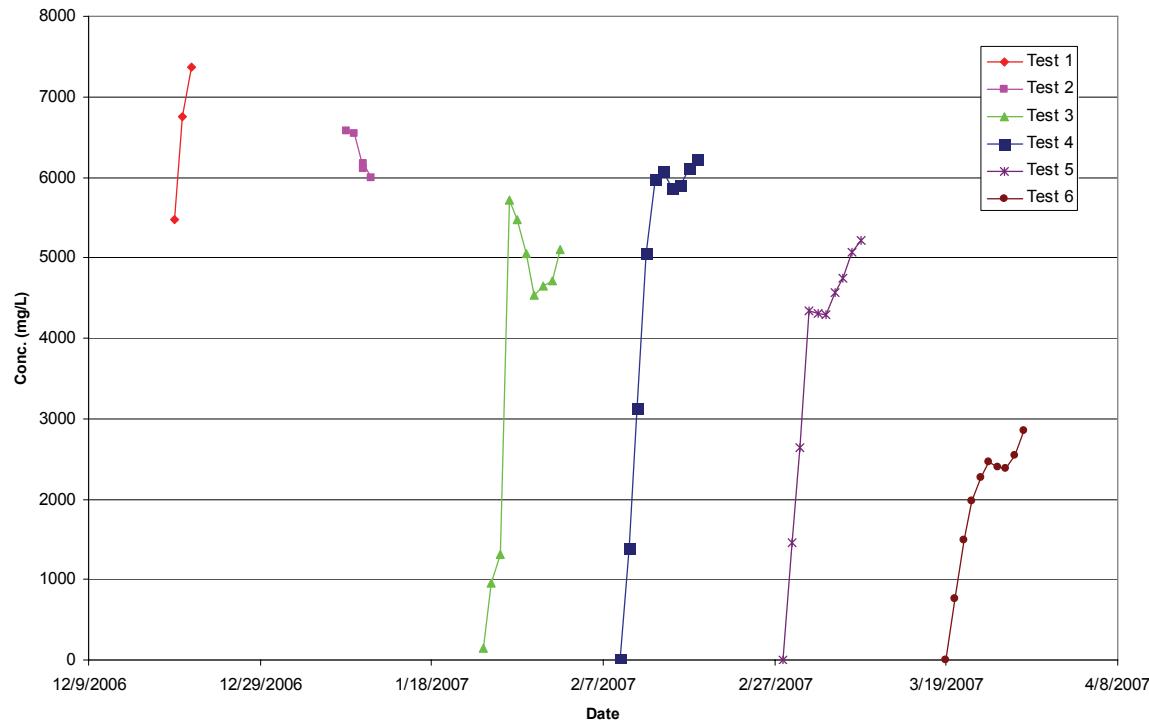
Uranium Dissolution



| Test | Initial U-238 in Test (g) | Dissolved U-238 (g) | % Dissolved U-238 | U-238 Xferred to V1 / PPT in V2 (g) |
|---------------------------|---------------------------|---------------------|-------------------|-------------------------------------|
| Test 1 (50 °C w/ mixing) | 25.08 | 25.02 | 99.76 | 9.04 |
| Test 2 (75 °C w/ mixing) | 25.08 | 24.81 | 98.92 | 5.73 |
| Test 3 (25 °C w/ mixing) | 25.08 | 24.98 | 99.60 | 5.76 |
| Test 4 (50 °C w/o mixing) | 25.08 | 24.92 | 99.38 | 5.75 |
| Test 5 (75 °C w/o mixing) | 25.08 | 24.76 | 98.72 | 8.95 |
| Test 6 (25 °C w/o mixing) | 25.08 | 24.87 | 99.17 | 5.74 |

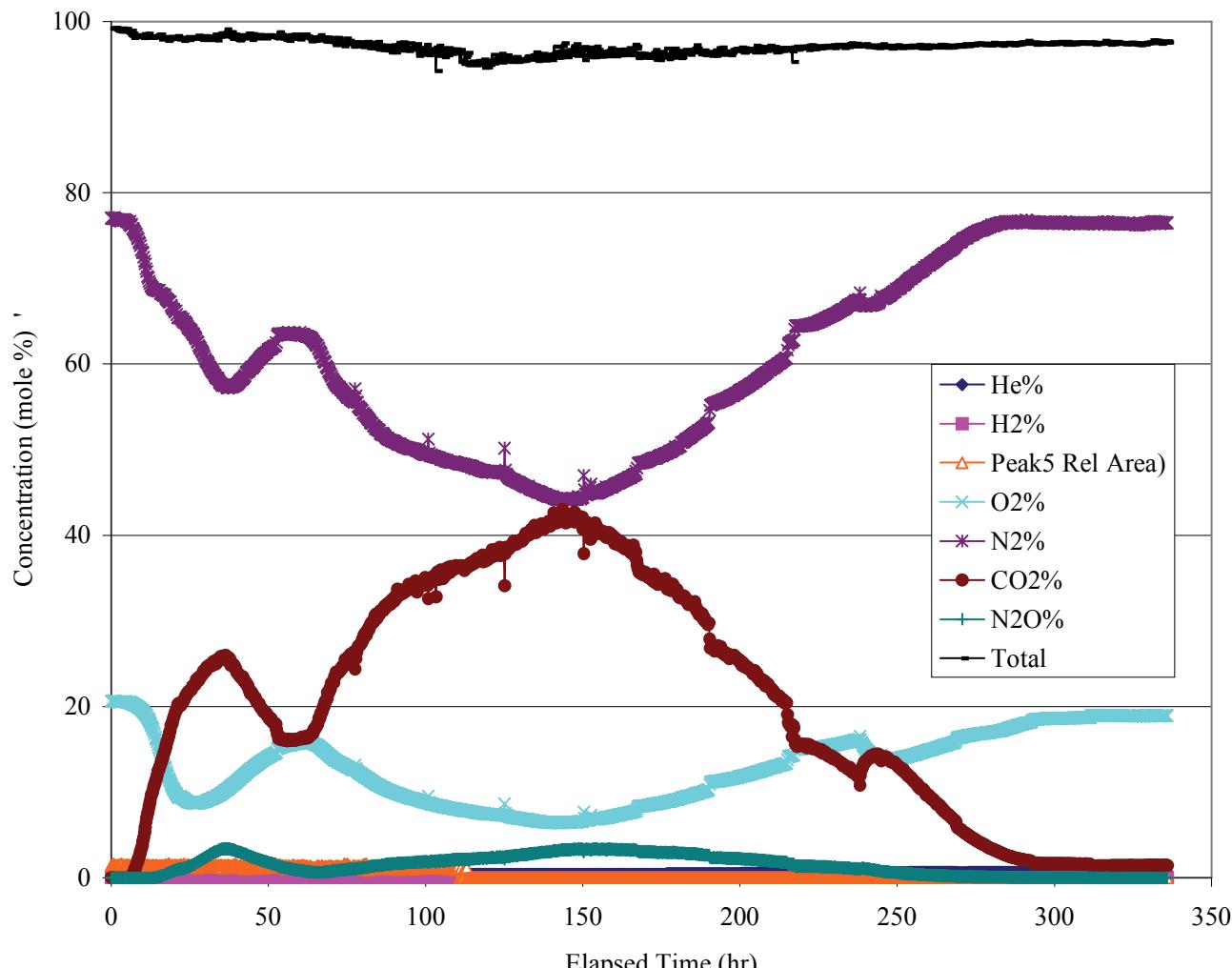
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Iron Dissolution

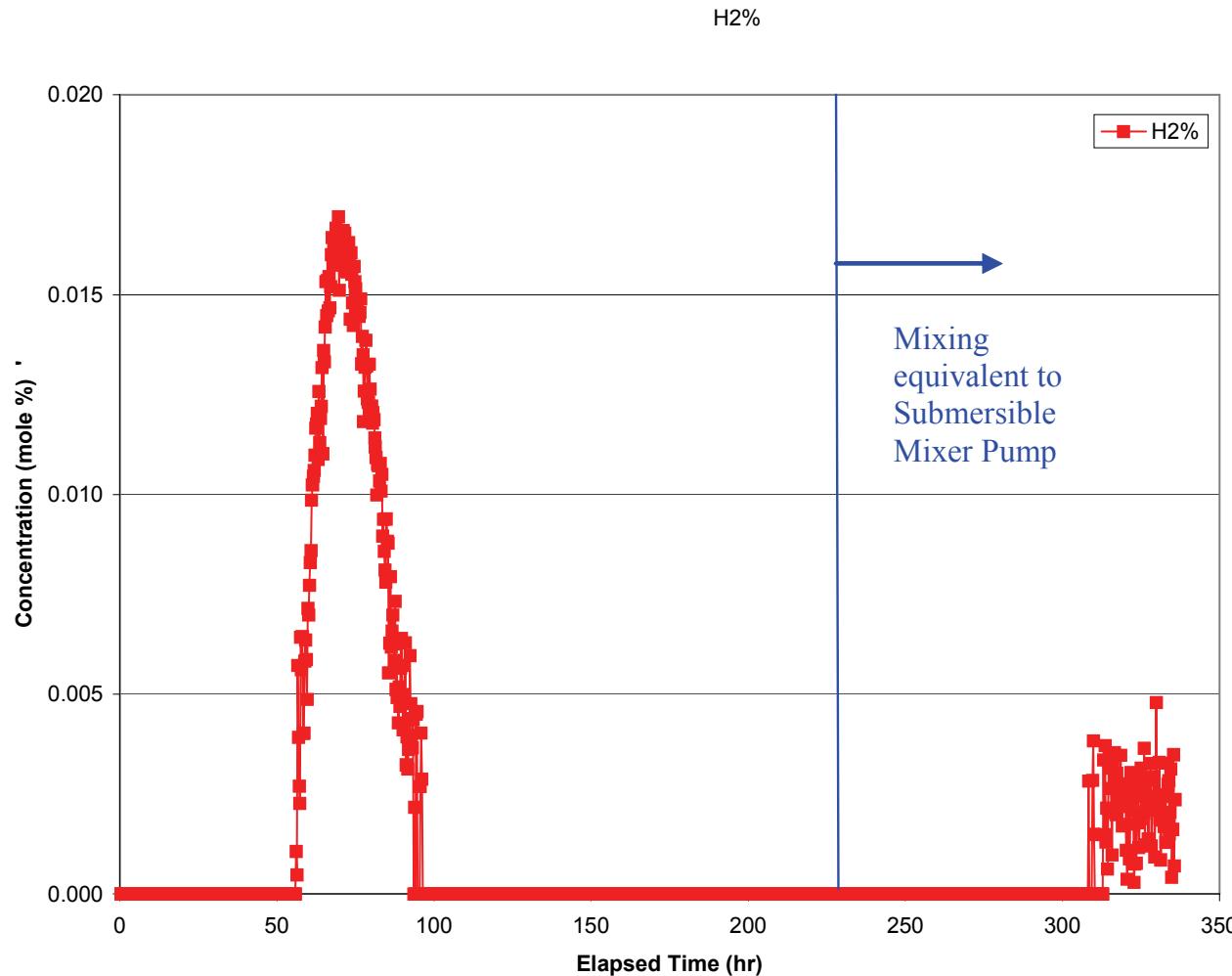


| Test | Initial Fe in Test (g) | Dissolved Fe (g) | % Fe Dissolved | Fe Xferred to V1 / PPT in V2 (g) |
|---------------------------|------------------------|------------------|----------------|----------------------------------|
| Test 1 (50 °C w/ mixing) | 39.33 | 39.04 | 99.26 | 14.11 |
| Test 2 (75 °C w/ mixing) | 39.33 | 36.81 | 93.59 | 8.49 |
| Test 3 (25 °C w/ mixing) | 39.33 | 39.11 | 99.44 | 9.02 |
| Test 4 (50 °C wo/ mixing) | 39.33 | 37.58 | 95.55 | 8.67 |
| Test 5 (75 °C wo/ mixing) | 39.33 | 38.66 | 98.30 | 13.97 |
| Test 6 (25 °C wo/ mixing) | 39.33 | 39.27 | 99.86 | 9.06 |

Composition of Gas from Dissolution Vessel of Test 4 (50 °C, unmixed)



Hydrogen (mol %) in gas from Dissolution Vessel in Test 4 (50 °C, unmixed)

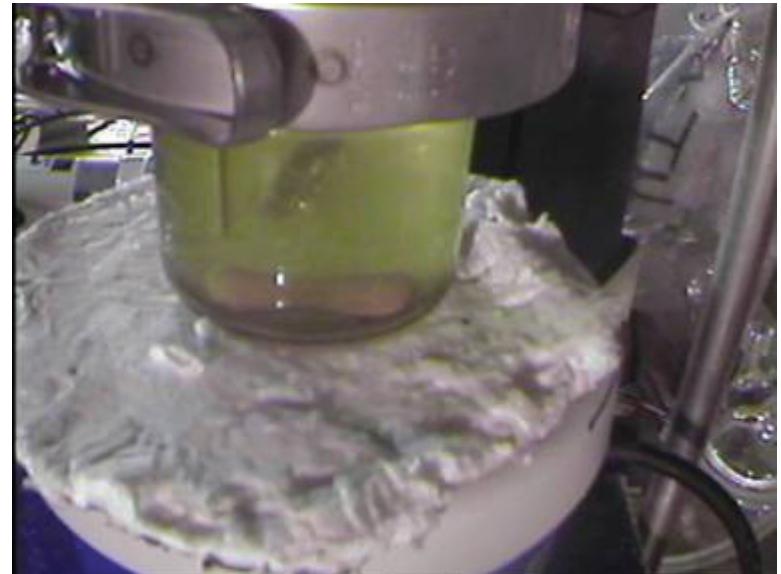


Actual Sludge Heel Oxalic Acid Cleaning Test

- 7 mL of sludge/supernate (~50/50 by wt)
- 140 mL of 8 wt % oxalic acid (20:1 OA to Slurry)
- 1/2" x 3/4" x 1/8" carbon steel coupon
- Two test temperatures: 50 °C and 75 °C
- Test scaled to protect Shielded Cells DSA limits
- Single batch addition of oxalic acid at start of test
- Slow stirring
- Continuous air purge to GC (10 – 50 cc/min)
- Hydrogen detection limit ~5 ppm

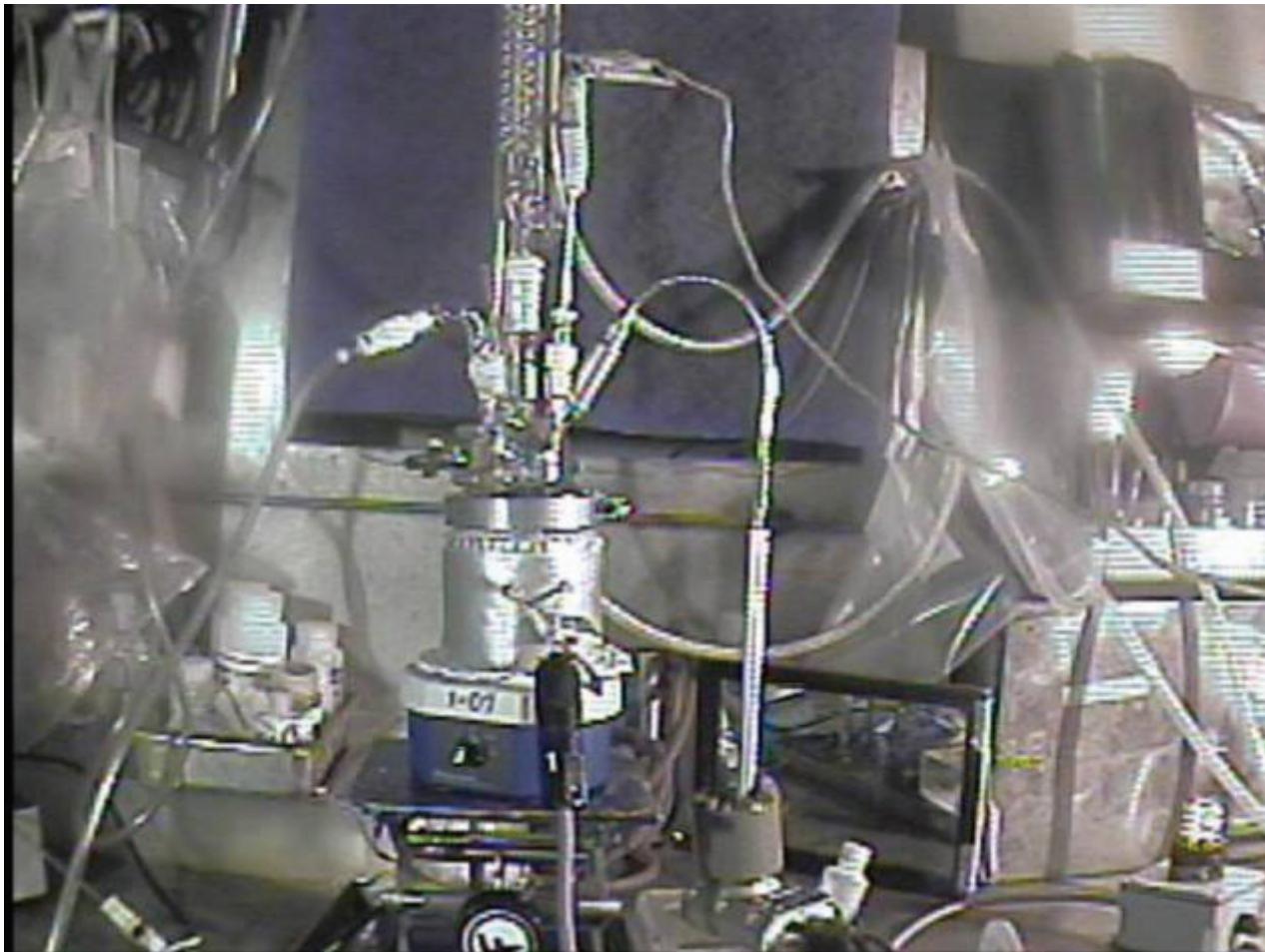
Actual Sludge Heel Oxalic Acid Cleaning Test

- Variants from actual process:
 - Batch addition of OA
 - much higher mixing energy
 - faster transfer rate
 - ~2X metal surface area to acid ratio
 - ~130X oxygen (air) turnover rate
- Test design:
 - 50 °C and 75 °C
 - Mixed
 - Measure hydrogen and other gases in off-gas, dissolution behavior, viscosity of slurry, characterization of solid residues

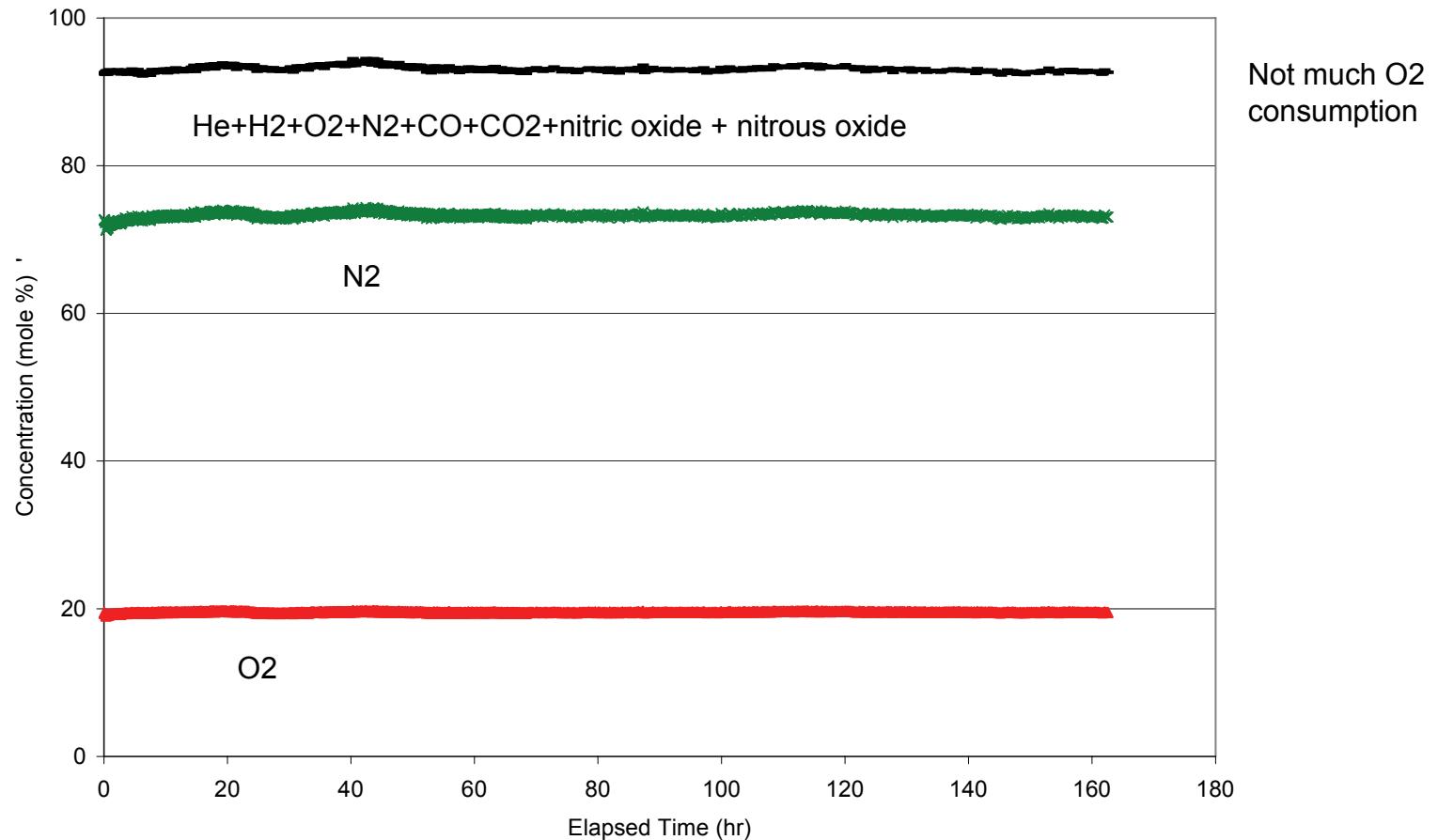


Post Dissolution View of Tank 5F Slurry

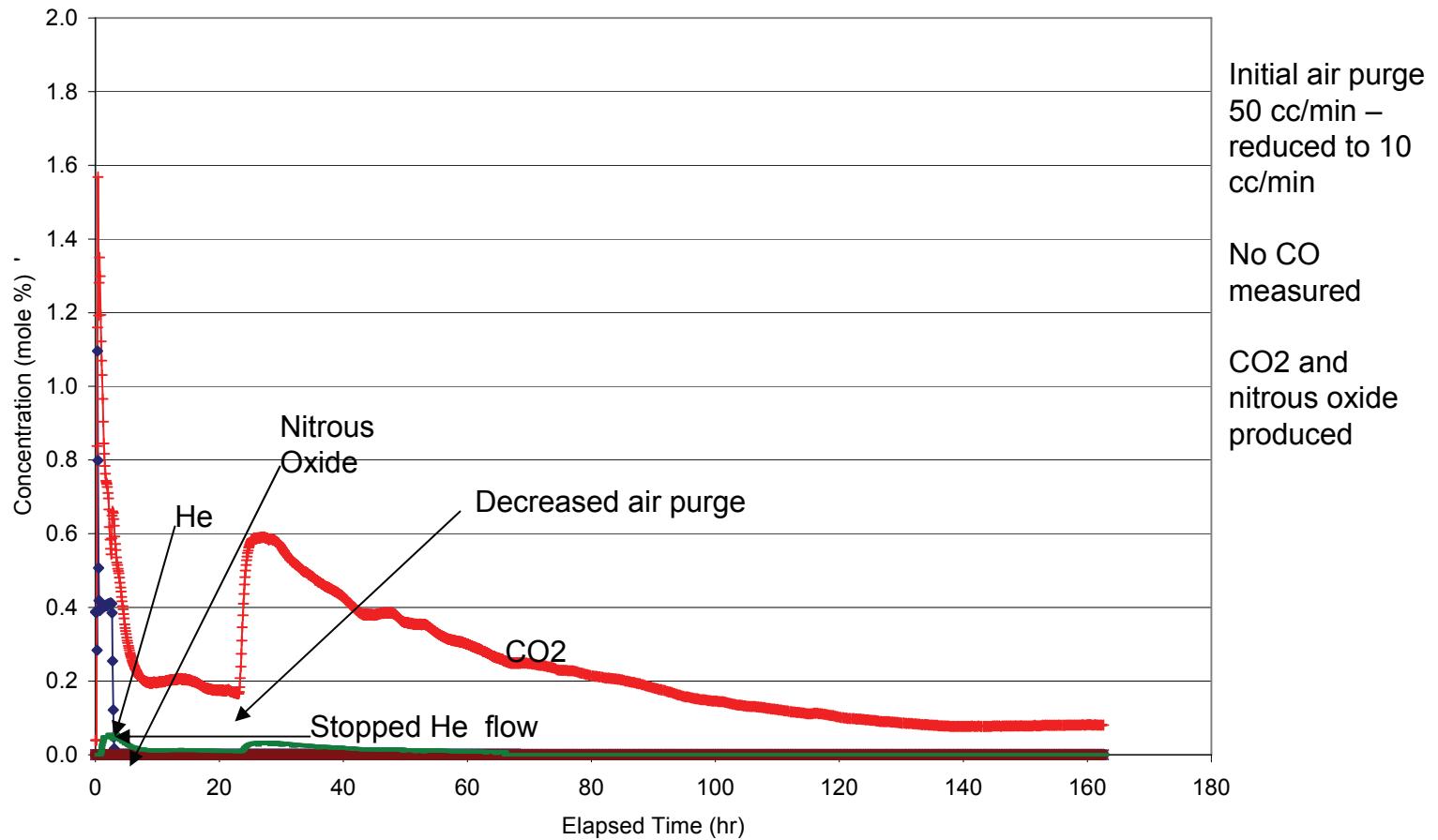
Chemical Cleaning Test In-Cell Equipment Setup



Test #1: Actual Waste, 50 °C



Test #1: Actual Waste, 50 °C



Dissolution of Sludge Heel During Test

Estimated Percentage of Key Elements Dissolved from the Tank 5F Sludge during Tank Cleaning Tests based on Oxalic Acid Analysis

| Analyte | Percentage Dissolved in 50 °C Test | Percentage Dissolved in 75 °C Test |
|-----------------------|---------------------------------------|---------------------------------------|
| Fe | 62 | 76 |
| U | 73 | 87 |
| Mn | 40 | 59 |
| Ni | 0.1 | 0.1 |
| Na | 96 | 95 |
| Al | 84 | 107 |
| ^{238}Pu | 2.9 | 2.9 |
| $^{239/240}\text{Pu}$ | 3.2 | 2.9 |

Neutralization of Oxalic Acid Solution

- Conducted neutralization tests at ambient temperature on filtered oxalic acid solutions from 50 °C and 75 °C cleaning tests
- For 50 °C Test Oxalic Acid Solution
 - Addition of solution to receipt tank simulated supernate via syringe - no layer formation
- For 75 °C Test Oxalic Acid Solution
 - Slow addition using modified pump - several layers formed
 - Layers easily mixed together
- Large volume of solids formed in both tests ($\text{Na}_2\text{C}_2\text{O}_4$)
- Solids from each test analyzed

Neutralization of Oxalic Acid Solution

- Analysis indicates most of the iron, uranium, manganese, and aluminum precipitated in both tests
- CSEM showed differences in particle size/morphology between two tests (rate of base addition?)
- 50 °C Test (fast addition) showed larger particles
- Some evidence of uranium separation in 75 °C Test, but also found in the original sludge.

Gas Generation during Chemical Cleaning

- Volume of gas generated during chemical cleaning normalized by volume of oxalic acid
 - 2.1 – 14.2 ft³ gas/ft³ oxalic acid
- Volume of hydrogen generated normalized by sludge volume and metal surface area
 - 0.00005 – 0.0012 ft³ hydrogen/kg sludge
 - 0.00002 – 0.0010 ft³ hydrogen/ft² surface area
- Projected gas generation during chemical cleaning
 - 28,000 – 189,000 ft³
- Projected hydrogen generation during chemical cleaning
 - 0.15 – 8.9 ft³

Conclusions

- Sludge heel is primarily PUREX sludge, high uranium
- “Snowbank” material is water soluble sodium carbonate and bicarbonate that will wash out
- Hydrogen concentration reached a maximum value of 0.017 vol %.
 - close to or below the detection limit (~5 ppm) for the gas chromatographs
- Gas composition was dominated by CO₂ formed from the corrosion reactions
- Amount of sludge dissolved varied between 60% and 99%
- Mass of residual solids in the Dissolution Vessel ranged between 31% and 51% of original sludge (primarily oxalate)
- Mass of solids formed in the Receipt Vessel (e.g., Tank 7F) ranged between 60% and 143% of the starting mass of sludge
- Floating precipitate layer in formed in the Receipt Vessel
- Evidence of minor amounts of separation of uranium from the poisons during the dissolution and re-precipitation process

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Q & A

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